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That I am knowledgeable in the English and Japanese languages, and that I believe that the English translation of the Japanese application No. 2002-222510 filed on July 31, 2002 attached hereto is a true and complete translation of the above-identified Japanese application as filed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.


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[Title of Document]

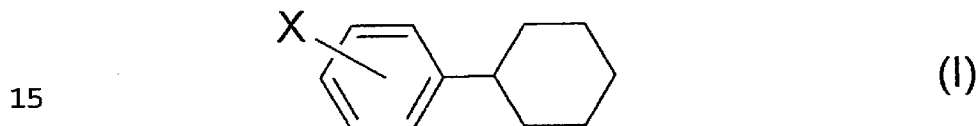
Specification

[Title of Invention]

5       Nonaqueous Electrolytic Solution and Lithium Secondary Battery Employing Same

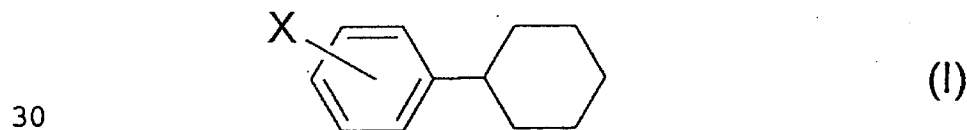
[What Is Claimed Is]

10       [Claim 1]       A nonaqueous electrolytic solution having an electrolyte dissolved in a nonaqueous solvent, wherein 0.1 to 20 wt.% of a cyclohexylbenzene having the following formula (I):



20       in which X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and the halogen atom is attached to an optional position of a benzene ring, is contained in the nonaqueous electrolytic solution.

25       [Claim 2]       A lithium secondary battery comprising a positive electrode, a negative electrode and a nonaqueous electrolytic solution having an electrolyte dissolved in a nonaqueous solvent, wherein 0.1 to 20 wt.% of a cyclohexylbenzene having the following formula (I):



35       in which X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and the halogen atom is attached to an optional position of a benzene ring, is contained in the nonaqueous electrolytic solution.

[Field of Invention]

The present invention relates to a nonaqueous electrolytic solution which can provide a lithium secondary battery having excellent battery characteristics in cycle performance, electric capacity and storage property, and a lithium secondary battery employing the solution.

[Prior Art]

Recently, a lithium secondary battery is generally employed as an electric source for driving small electronic devices. The lithium secondary battery essentially comprises a positive electrode, a nonaqueous electrolytic solution, and a negative electrode. A lithium secondary battery utilizing a positive electrode of lithium compound oxide such as  $\text{LiCoO}_2$  and a negative electrode of carbonaceous material or lithium metal is favorably used. As nonaqueous electrolytic solution for the lithium secondary battery, a carbonate such as ethylene carbonate (EC) or propylene carbonate (PC) is favorably used.

[Problems to be Solved by Invention]

Nevertheless, it is desired to provide a secondary battery showing improved characteristics in the cycle performance and electric capacity.

A lithium secondary battery utilizing a positive electrode of  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  or  $\text{LiNiO}_2$  sometimes shows decrease of electric performances because a portion of the solvent in the nonaqueous electrolytic solution oxidatively decomposes in the course of charging and hence the produced decomposition product disturbs the desired electrochemical reaction. The decomposition is considered to be caused by electrochemical oxidation of the solvent on the interface between the positive electrode and the nonaqueous electrolytic solution.

On the other hand, a lithium secondary battery utilizing a negative electrode of carbonaceous material of high crystallization such as natural graphite or artifi-

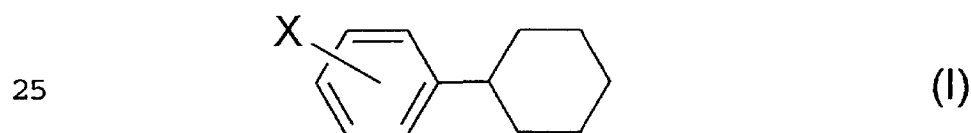
cial graphite also shows decrease of electric performances because a solvent of the nonaqueous electrolytic solution reductively decomposes on the surface of the negative electrode in the course of charging. The reductive decomposition also occurs in the repeated charging-discharging procedures when EC which is generally employed as the nonaqueous solvent of the electrolytic solution is utilized as the nonaqueous solvent.

For these reasons, battery characteristics in the cycle performance and electric capacity are not satisfactory.

The present invention has an object to provide a nonaqueous electrolytic solution which can produce a lithium secondary battery showing improved battery cycle performance, improved electric capacity, and improved storage property in the charged condition, and a lithium secondary battery employing the solution.

[Means for Solving Problems]

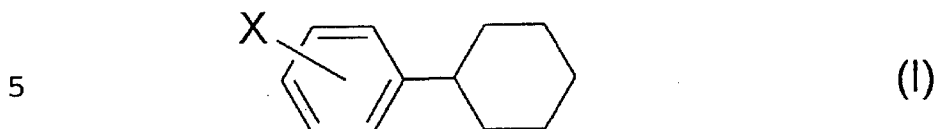
The present invention relates to a nonaqueous electrolytic solution having an electrolyte dissolved in a nonaqueous solvent, wherein 0.1 to 20 wt.% of a cyclohexylbenzene having the following formula (I):



in which X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and the halogen atom is attached to an optional position of a benzene ring, is contained in the nonaqueous electrolytic solution.

The present invention further relates to a lithium secondary battery comprising a positive electrode, a negative electrode and a nonaqueous electrolytic solution having an electrolyte dissolved in a nonaqueous solvent,

wherein 0.1 to 20 wt.% of a cyclohexylbenzene having the following formula (I):



in which X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and the halogen atom is attached to an optional position of a benzene ring, is contained in the nonaqueous electrolytic solution.

[Preferred Embodiments of Invention]

15 In the cyclohexylbenzene represented by the formula (I) and contained in the nonaqueous electrolytic solution containing an electrolyte dissolved in a nonaqueous solvent, X represents a halogen atom selected from a group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom. The halogen atom preferably is a fluorine atom, a chlorine atom or bromine atom, and more preferably is a fluorine atom or chlorine atom.

25 Examples of the cyclohexylbenzenes represented by the formula (I) include 1-fluoro-2-cyclohexylbenzene, 1-fluoro-3-cyclohexylbenzene, 1-fluoro-4-cyclohexylbenzene, 1-chloro-4-cyclohexylbenzene, 1-bromo-4-cyclohexylbenzene, and 1-iodo-4-cyclohexylbenzene.

30 If the content of the cyclohexylbenzene in the nonaqueous electrolytic solution is extremely large, the battery performances may lower. If the content of the cyclohexylbenzene is extremely small, an expected improvement of the battery performances cannot be attained. Accordingly, the content preferably is in the range of 0.1-20 wt.%, more preferably 0.2-10 wt.%, most preferably 35 0.5-5 wt.%, based on the amount of the nonaqueous electrolytic solution, so that the cycle performance can be

well improved.

Examples of the non-aqueous solvents employed in the invention are cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and vinylene carbonate (VC), lactones such as  $\gamma$ -butyrolactone, linear carbonates such as dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), and diethyl carbonate (DEC), ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane and 1,2-dibutoxyethane, nitriles such as acetonitrile, esters such as methyl propionate, methyl pivalate and octyl pivalate, and amides such as dimethylformamide.

The non-aqueous solvents can be employed singly or in combination of two or more. There are no specific limitations with respect to the combination of the non-aqueous solvents. Examples of the combinations include a combination of a cyclic carbonate and a linear carbonate, a combination of a cyclic carbonate and a lactone, and a combination of plural cyclic carbonates and linear carbonates.

Examples of the electrolytes employed in the invention include  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiPF}_4(\text{CF}_3)_2$ ,  $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ ,  $\text{LiPF}_3(\text{CF}_3)_3$ ,  $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)_3$ , and  $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)$ . These electrolytes can be employed singly or in combination of two or more. The electrolyte can be incorporated into the nonaqueous solvent generally in such an amount as to give an electrolytic solution of 0.1 M to 3 M, preferably 0.5 M to 1.5 M.

The electrolytic solution of the invention can be prepared, for instance, by mixing the above-mentioned non-aqueous solvents; dissolving the above-mentioned electrolyte in the mixture; and further dissolving at least one of the above-mentioned cyclohexylbenzenes having the formula (I) in the resulting mixture.

The nonaqueous electrolytic solution can be employed as material of the lithium secondary battery. Other materials than the nonaqueous electrolytic solution are not limited and conventionally employed materials can be employed.

For instance, the active material of positive electrode is a compound metal oxide comprising lithium and cobalt or nickel. The active material of positive electrode can be used singly or in combination. Examples of the compound metal oxides include  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$  ( $0.01 < x < 1$ ). These compounds can be employed in an optional combination such as a combination of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$ , a combination of  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ , and a combination of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNiO}_2$ .

The positive electrode can be manufactured by kneading the above-mentioned active material of positive electrode, an electro-conductive material such as acetylene black or carbon black, and a binder such as poly(tetrafluoroethylene) (PTFE) or poly(vinylidene fluoride) (PVDF), to give a positive electrode composition; coating the positive electrode composition on a collector such as aluminum foil or a lath plate of stainless steel; drying and pressing the coated composition, and heating the pressed composition *in vacuo* at a temperature of approximately 50 to 250°C for approximately 2 hours.

Examples of the active material of negative electrode include lithium metal, lithium alloy and carbonaceous material having crystal structure of graphite type and capable of absorbing and releasing lithium [thermally decomposed carbons, cokes, graphites (such as artificial graphite and natural graphite), fired organic polymer, carbon fiber] and complex tin oxide. It is preferred to employ artificial graphite and natural graphite having a graphite crystal structure in which the lattice distance of lattice surface (002), namely,  $d_{002}$ , is in the range of 0.335 to 0.340 nm. The active materials of negative

electrode can be employed singly or in combination. A powdery material such as the carbonaceous material is preferably used in combination with a binder such as ethylene propylene diene terpolymer (EPDM), poly(tetra-  
5 fluoroethylene) (PTFE) or poly(vinylidene fluoride) (PVDF). There are no limitations with respect to the preparing method of the negative electrode. The negative electrode can be prepared by a method similar to that for the preparation of the positive electrode.

10 There are no specific limitations with respect to the structure of the lithium secondary battery of the invention. For instance, the lithium secondary battery can be a battery of coin type comprising a positive electrode, a negative electrode, and single or plural separa-  
15 tors, or a cylindrical or prismatic battery comprising a positive electrode, a negative electrode, and a separator roll. The separator can be a known material such as micro-porous polyolefin film, woven cloth, or non-woven cloth.

20 [Examples]

The present invention will be further described with reference to examples and comparison examples.

[Example 1]

[Preparation of nonaqueous electrolytic solution]

25 In a nonaqueous solvent of EC:DEC (=3:7, volume ratio) was dissolved 1M of  $\text{LiPF}_6$  to give a nonaqueous electrolytic solution. To the nonaqueous electrolytic solution was further added 2.0 wt.% of 1-fluoro-4-cyclohexylbenzene based on the amount of the nonaqueous electrolyt-  
30 ic solution.

[Manufacture of lithium secondary battery and measurement of its battery performances]

$\text{LiCoO}_2$  (positive electrode active material, 80 wt.%), acetylene black (electro-conductive material, 10 wt.%),  
35 and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added 1-

5 methyl-2-pyrrolidone. Thus produced mixture was coated on aluminum foil, dried, pressed, and heated to give a positive electrode. Artificial graphite (negative electrode active material, 90 wt.%) and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added 1-methyl-2-pyrrolidone. Thus produced mixture was coated on copper foil, dried, pressed, and heated to give a negative electrode. The positive and negative electrodes, a microporous polypropylene film separator, and the above-mentioned non-aqueous electrolytic solution were employed to give a coin-type battery (diameter: 20 mm, thickness: 3.2 mm).

10 The coin-type battery was charged at room temperature (20°C) with a constant electric current (0.8 mA) to reach 4.2 V (terminal voltage) for 5 hours. Subsequently, the battery was discharged to give a constant electric current (0.8 mA) to give a terminal voltage of 2.7 V. The charging-discharging cycle procedure was repeated. The initial charge-discharge capacity was almost the same as the capacity measured in a battery using an 1M LiPF<sub>6</sub> and EC/DEC (3/7, volume ratio) solvent mixture (containing no additive) [see Comparison Example 1]. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 92.9% of the initial discharge capacity (100%). The low temperature performances are also good. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 2]

30 The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 5.0 wt.% of 1-fluoro-4-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 91.4%. The conditions for manufac-

turing the coin-type battery and the battery performances are shown in Table 1.

[Example 3]

5 The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 0.5 wt.% of 1-fluoro-4-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 90.5%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Comparison Example 1]

15 In a non-aqueous solvent of EC:DEC (=3:7, volume ratio) was dissolved 1 M of  $\text{LiPF}_6$  to give a nonaqueous electrolytic solution. To the nonaqueous electrolytic solution was added no cyclohexylbenzene compound. Then, a coin-type battery was manufactured by employing the resulting nonaqueous electrolytic solution in the same manner as in Example 1. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 82.6% of the initial discharge capacity. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

25 [Example 4]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 2.0 wt.% of 1-fluoro-2-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 92.4%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

35 [Example 5]

The procedures of Example 1 for preparing a nonaque-

ous electrolytic solution and manufacturing a coin-type battery were repeated except for using 2.0 wt.% of 1-fluoro-3-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 92.0%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 6]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 2.0 wt.% of 1-chloro-4-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 89.1%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 7]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 2.0 wt.% of 1-bromo-4-cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 88.9%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Comparison Example 2]

The procedures of Example 2 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 5.0 wt.% of fluoro-benzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 82.9%. The conditions for manufacturing the coin-type battery

and the battery performances are shown in Table 1.

[Comparison Example 3]

The procedures of Example 2 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for using 5.0 wt.% of cyclohexylbenzene based on the amount of the nonaqueous electrolytic solution. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 83.1%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 8]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for replacing the artificial graphite with natural graphite as active material of the negative electrode. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 92.6%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 9]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for replacing the  $\text{LiCoO}_2$  with  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  as active material of the positive electrode. After the 50 cycle charging-discharging procedure, the retention of discharge capacity was 91.0%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

[Example 10]

The procedures of Example 1 for preparing a nonaqueous electrolytic solution and manufacturing a coin-type battery were repeated except for replacing the  $\text{LiCoO}_2$  with  $\text{LiMn}_2\text{O}_4$  as active material of the positive electrode. After the 50 cycle charging-discharging procedure, the

retention of discharge capacity was 92.4%. The conditions for manufacturing the coin-type battery and the battery performances are shown in Table 1.

5

Table 1

Exam- ple	Electrode Posi. Nega.	Additive (amount: wt.%)	Electro- lytic solution	Initial capacity (r.v.)	50% cycle retention (%)
10					
15	1 LiCoO <sub>2</sub> Art.	1-fluoro-4- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.02	92.9
20	2 LiCoO <sub>2</sub> Art.	1-fluoro-4- cyclohexyl- benzene (5.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.01	91.4
25	3 LiCoO <sub>2</sub> Art.	1-fluoro-4- cyclohexyl- benzene (0.5)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.01	90.5
30	Com. 1 Art.	LiCoO <sub>2</sub> None	1M LiPF <sub>6</sub> EC/DEC =3/7	1.00	82.6
35	4 LiCoO <sub>2</sub> Art.	1-fluoro-2- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.02	92.4
40	5 LiCoO <sub>2</sub> Art.	1-fluoro-3- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.02	92.0
	6 LiCoO <sub>2</sub>	1-chloro-4-	1M LiPF <sub>6</sub>	1.01	89.1

		Art.	cyclohexyl- benzene (2.0)	EC/DEC =3/7		
5	7	LiCoO <sub>2</sub> Art.	1-bromo-4- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.01	88.9
10	2	Com. LiCoO <sub>2</sub> Art.	fluoro- benzene (5.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	0.99	82.9
15	3	Com. LiCoO <sub>2</sub> Art.	cyclohexyl- benzene (5.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	0.99	83.1
20	8	LiCoO <sub>2</sub> Nat.	1-fluoro-4- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.02	92.6
25	9	LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub> Art.	1-fluoro-4- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	1.14	91.0
30	10	LiMn <sub>2</sub> O <sub>4</sub> Art.	1-fluoro-4- cyclohexyl- benzene (2.0)	1M LiPF <sub>6</sub> EC/DEC =3/7	0.99	92.4

Remarks:

- 35      Posi : positive electrode  
          Nega : negative electrode  
          Art : artificial graphite  
          Nat : natural graphite

- 40      The present invention is not limited to the above  
          examples and various thinkable combinations based on the  
          gist of the invention can be employed. Particularly,

there is no limitation with respect to the combinations of the solvents. The above examples describe a battery of coin type. However, the present invention can be applied for a cylindrical or prismatic battery.

5           [Effect of Invention]

The present invention can provide a lithium secondary battery having excellent battery characteristics in cycle performance, electric capacity and storage property.

10

[Title of Document]

Sheet for Summary

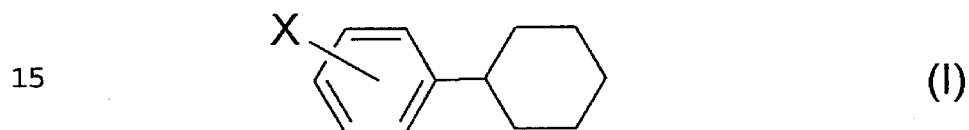
[Summary]

[Object]

- 5        A lithium secondary battery having excellent battery characteristics in cycle performance, electric capacity and storage property can be provided.

[Solving Means]

- 10       The present invention relates to a nonaqueous electrolytic solution having an electrolyte dissolved in a nonaqueous solvent, wherein 0.1 to 20 wt.% of a cyclohexylbenzene having the following formula (I):



- in which X is a halogen atom selected from the group consisting of a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, and the halogen atom is attached to an optional position of a benzene ring, is contained in the nonaqueous electrolytic solution, and relates to a lithium secondary battery employing the above nonaqueous electrolytic solution.

- 25       [Selected Drawing]

None